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## **DISPERSANTS: A REVIEW OF EFFECTIVENESS MEASURES AND STUDIES**

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### **INTRODUCTION**

Dispersants have generated the greatest amount of studies and discussion since the birth of the oil spill industry twenty years ago after the TORREY CANYON incident. Discussion is still as lively today and there still exists a polarization between dispersant proponents and opponents. Little has changed in the way of documentation. There is still no undisputed documentation on large-scale experiments or use to show that dispersants are effective or not. Similarly, no large scale biological experiments have convinced all environmentalists that the use of dispersants is safe in all conditions, although the evidence is becoming increasingly clear that dispersants cause little ecological damage above that by un-treated oil and that they could in fact minimize ecological damage if they were effective.

The active ingredient in dispersants are surface active agents or surfactants. Surfactants have varying solubility in water and have varying actions toward oil and water. One parameter that has been used to characterize surfactants is the HLB or the hydrophilic-lipophilic balance.<sup>1</sup> A surfactant with an HLB of about 1 to 8 promotes the formation of water-in-oil emulsions and one with an HLB in the range of 12 to 20 promotes the formation of oil-in-water emulsions. Dispersants have HLB's in the range of 9 to 11. The HLB range as defined is only applicable to non-ionic surfactants, however ionic surfactants can be rated using an expanded scale and often have HLB's ranging from 25 to 40. They are strong water-in-oil emulsifiers, very soluble in water, relatively insoluble in oil, and generally work from the water to any oil present. Such products have little applicability to oil on water because they rapidly disappear in the water column, having little effect on oil. However, because of their commonality and cheapness many ionic-surfactants are proposed as dispersants. It is these agents, that should be better classed as surface-washing agents.

Surface-washing agents then are surfactant-containing mixtures with high HLB's and are best suited to removing oil from solid surfaces such as shorelines, roads and parking lots. EETD has developed an effectiveness test for such agents and results of these tests are reported in the literature. Many such agents come onto the market each year, many are re-packaged industrial cleaners and have little utility in spills.

### **DISPERSANTS - FIELD EFFECTIVENESS TRIALS**

Over the past 12 years, 107 test spills have been laid out to test the effectiveness of oil spill dispersants.<sup>2</sup> These spills are summarized in Table 1. A number of smaller tests or other tests which were not documented have taken place but are not included here. Of the 107 slicks documented, 23 are controls used to establish a comparison. Percentage effectiveness is reported in 25 spills and the average for these is 30%. Values range from 0 to 100%. Most experimenters have not assigned effectiveness values because, as will be demonstrated in more depth later, effectiveness values are hard to assign.

The test results show clearly that dispersants are not highly effective, even under

highly controlled experimental situations. Of greater concern than this is the methodology used to estimate effectiveness. Some experimenters simply estimated effectiveness, but most based their measure on integrations of water column concentrations relative to surface slick dimensions. This is not a correct means to perform the measure because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different than surface dynamics. Extreme cases of the positional variances between surface and sub-surface slicks have been illustrated by Brown and Goodman in controlled tank testing.<sup>3</sup> Their work has shown that the underwater plumes move in highly random fashions with respect to the surface slick and even two trials conducted on the same day will not have similar movement patterns.

TABLE 1.—Data from dispersant effectiveness trials.\*

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount, m <sup>3</sup>	Dispersant	Application Method	Dose Rate, l/d	Sea State	Claimed Effectiveness, %
North Sea	Cormack and Nichols [1,2]	1976	1	Ekofisk	0.5	10% conc.	ship, WSL	...	1	...
Wallops Island	McAuliffe et al. [1,3]	1978	2	Kuwait	...	10% conc.	ship, WSL	1:20	2-3	100
			3	Murban	1.7	Corexit 9527	helicopter	1:5	1	...
			4	La Rosa	1.7	Corexit 9527	helicopter	1:5	1	...
South California	Smith et al. [4]	1978	5	Murban	1.7	Corexit 9527	helicopter	1:11	1	100
			6	La Rosa	1.7	Corexit 9527	helicopter	1:11	1	50
			7	North Slope	1.7	Control later Corexit 9527	control then helicopter	> 1:5	0-1	...
			8	North Slope	3.2	Corexit 9527	airplane, Cessna	> 1:5	0-1	...
			9	North Slope	1.7	Recovery + Corexit 9527	helicopter	> 1:5	0-1	...
			10	North Slope	0.8	BP1100WD	ship, WSL	> 1:5	0-1	...
			11	North Slope	0.8	Corexit 9527	ship	> 1:5	0-1	...
South California	Smith et al. [4]	1978	12	North Slope	3.2	Corexit 9527	airplane, Cessna	> 1:5	1-2	...
			13	North Slope	0.8	Corexit 9527	ship	> 1:5	1-2	...
			14	North Slope	0.8	BP1100WD	ship, WSL	> 1:5	1-2	...
			15	North Slope	0.6	several, demonstration	several, demonstration	...	1-2	...
Victoria	Green et al. [1,6]	1978	16	North Slope	0.2	10%, 9527	ship, WSL	1:1	2	...
			17	North Slope	0.4	10%, 9527	ship, WSL	1:1	1	...
			18	North Slope	0.2	10%, 9527	ship, WSL	1:1	1	...

TABLE I—(cont'd.).

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount, m <sup>3</sup>	Dispersant	Application Method	Dose Rate, D:O	Sea State	Claimed Effectiveness, %
Long Beach	McAuliffe et al. [1,5]	1979	19	Prudhoe Bay	1.6	control	control	...	2-3	0.5
			20	Prudhoe Bay	1.6	2% conc.	ship	1:67	2-3	8
			21	Prudhoe Bay	1.6	2% conc.	ship	1:67	2-3	5
			22	Prudhoe Bay	3.2	conc.	airplane, DC-4	1:20	2-3	78
Long Beach	McAuliffe et al. [1,5]	1979	23	Prudhoe Bay	1.6	conc.	airplane, DC-4	1:25	2-3	45
			24	Prudhoe Bay	1.6	control	control	...	2-3	1
			25	Prudhoe Bay	3.2	conc.	airplane, DC-4	1:27	2-3	60
			26	Prudhoe Bay	1.6	2%	ship	1:11	2-3	11
			27	Prudhoe Bay	1.6	2%	ship	1:11	2-3	62
Mediterranean, Protecmar I	Bocard et al. [7]	1979	28-41	light fuel	3 each	BP1100X BP1100WD Finasol OSR- 5 Corexit 9527	ship, helicopter, various and airplane CL215	...	1-3	...
Mediterranean, Protecmar II		1980	42-49	light fuel	1-5.5	BP1100X BP1100WD Finasol OSR- 5 Corexit 9527	ship, helicopter, various and airplane CL215	...	1-3	...
Mediterranean Protecmar III	Bocard and Gatellier [1,7,8]	1981	50	light fuel	6.5	Dispolene 325	airplane, CL215	1:3	1-2	50
Newfoundland	Gill et al. [9]	1981	51	light fuel	6.5	Shell	airplane, CL215	1:3	2-3	...
			52	light fuel	6.5	control	control	...	1-2	...
			53	ASMB	2.5	control	control	...	1	...
Norway	Lichtenthaler and Daling [1,10]	1982	54	ASMB	2.5	Corexit 9527	airplane, DC-6	1:10	1	...
			55	Statfjord	0.2	control	control	...	2-3	0.6
			56	Statfjord	0.2	10% conc.	ship	1:10	2-3	6
			57	Statfjord	0.2	10% conc.	ship	1:10	2-3	17
			58	Statfjord	0.2	control	control	...	2-3	2.6
			59	Statfjord	0.2	10% conc.	ship	1:17	2-3	19
			60	Statfjord	0.2	10% conc.	ship	1:18	2-3	22
			61	Statfjord	0.2	10% conc.	ship	1:13	2-3	2
North Sea	Cormack [1,11]	1982	62	Arabian	20	control	control	...	1	...
			63	Arabian	20	Corexit 9527	airplane, Islander	1:2	1	...
			64	Arabian	20	Corexit 9527	airplane, Islander	1:4	1	...
			65	light fuel	3	10% Dispolene 325	ship	1:2	3	...
Mediterranean Protecmar V	Bocard et al. [1,12]	1982	66	light fuel	5	Dispolene 325	airplane, CL215	1:2.4	3	...
Protecmar V	Bocard et al. [1,12]	1982	67	light fuel	5	Dispolene 325	ship	1:2.8	2	...
			68	light fuel	5	Dispolene 325	airplane, CL215	1:2.8	2	...
			69	light fuel	3.5	Dispolene 325	ship	1:2.6	1-2	...
			70	light fuel	4	Dispolene 325	helicopter	1:2.9	1-2	...
			71	light fuel	2	premixed	premixed	1:20	1-2	40-50
			72	light fuel	5	control	control	...	2	...
			73	Statfjord	2	control	control	...	1-2	2
			74	light fuel	2	control	control	...	1-2	2
Holland	Delvigne [1,13]	1983	75	Statfjord	2	control	control	...	1	2
			76	Statfjord	2	Finasol OSR-5	airplane	1:10-30	1	2
			77	light fuel	2	Finasol OSR-5	airplane	1:10-30	1	2
			78	Statfjord	2	Finasol OSR-5	premixed	1:20	2-3	100
			79	light fuel	2	control	control	...	2-3	2
			80	Statfjord	2	Finasol OSR-5	airplane	1:10-30	1-2	2
			81	Statfjord	2	Finasol OSR-5	airplane	1:10-30	1-2	2

TABLE 1—(cont'd.).

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount, m <sup>3</sup>	Dispersant	Application Method	Dose Rate, D:O	Sea State	Claimed Effectiveness, %
Halifax	Swiss and Gill [1,14,15]	1983	82	ASMB	2.5	Corexit 9527	helicopter	1:20	1	2.5
			83	ASMB	2.5	control	control	...	1	1
			84	ASMB	2.5	Corexit 9550	helicopter	1:10	1	13
			85	ASMB	2.5	control	control	...	1	1
			86	ASMB	2.5	BP MA700	helicopter	1:10	2-3	10-41
Norway	Lichtenthaler and Daling [16]	1984	87	ASMB	2.5	control	control	...	2-3	7
			88	Statfjord	10	control	control	...	1	...
			89	Statfjord	10	Corexit 9527	airplane, Islander	1:75	1	...
Norway	Lichtenthaler and Daling [16]	1984	90	Statfjord	10	control	control	...	2	...
			91	Statfjord	10	Corexit 9527	airplane	1:80	2	...
Brest, Protecmar VI	Bocard [7,17]	1985	92	Statfjord	12	Corexit 9527	premixed	1:33	2	...
			93	Statfjord	10	Corexit 9527	airplane	1:50	...	...
			94	fuel oil	5	control	control	...	1	...
			95	fuel oil	28	Dispolene 355	helicopter	1:9	1	...
			96	fuel oil	part of above	Dispolene 355	ship-spray	1:9	1	...
Haltienbanken	Sørstrøm [19]	1985	97	fuel oil	part of above	Dispolene 355	ship-acrosol	1:9	1	...
			98	topped Statfjord crude	12.5	control	...	...	1-2	...
			99	topped Statfjord crude	12.5	Finasol	premixed, injected 3 m below surface	1:50	1-2	...
			98	topped Statfjord crude	above 12.5	control	...	...	1-2	...
Haltienbanken	Sørstrøm [19]	1985	99	topped Statfjord crude	12.5	Finasol	premixed, injected 3 m below surface	1:50	1-2	...
			100	topped Statfjord crude	12.5	control	...	...	1-2	...
Beaufort Sea	Swiss et al. [20]	1986	101	topped Statfjord crude	12.5	alcopol (demulsifier)	premixed	250 ppm	1-2	...
			101 (CA)	topped Federated crude	2.5	control	...	...	1-2	...
			102 (CB)	topped Federated crude	2.5	control	...	...	1-2	...
			103 (C1)	topped Federated crude	2.5	BP MA700	helicopter	1:10	2-3	...
			104 (T1)	topped Federated crude	2.5	BP MA700	helicopter	1:1	2-3	...
			105 (T2)	topped Federated crude	2.5	Corexit CRX-8	helicopter	1:1	2-3	...
			106 (C)	topped Federated crude	2.5	control	...	...	2-3	...

\* Abbreviations: ASMB—Alberta Sweet Mixed Blend, conc.—concentrate, and WSL—Warren Springs Laboratory.

Furthermore, all of the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate and can result in effectiveness values that are much larger and range from twice to ten times greater than the actual values. In fact because dispersion only occurs from the thicker portions of the slick and because these only constitute about 10% of the slick surface area, the error in measurement is as great as a factor of 10 in two dimensions and as great as 10 times 10 or 100-fold in three dimensions or overall! Other errors in the opposite direction compensate for this somewhat, but the overall result is a large exaggeration of effectiveness.

Surface measures are also inadequate. Remote sensing does not provide a thickness measure and thus calculating volume is impossible. Numerous surface phenomena also interfere with the process of estimating slick volume. These have been detailed in a recent paper by Goodman and Fingas.<sup>4</sup> A new technique for measuring surface thickness is currently in development by Esso Resources Canada, Minerals Management Service, Environment Canada and the American Petroleum Institute. This instrument offers potential to measure effectiveness on the open ocean.

In summary, field trials of dispersant effectiveness have not shown any quantitative or qualitative proof of high (>50%) dispersant effectiveness. Analytical means do not exist at this time to accurately quantify dispersant effectiveness at field trial situations.

#### DISPERSANTS - ACTUAL USAGE

Table 2 lists dispersant usage during some notable large spills.<sup>5,6</sup> Results are summarized from the noted references. The problem with actual spill data is that some observers may have reported seeing evidence of effectiveness and others directly the opposite. In none of the cases were any analytical means tried to quantify effectiveness or even to provide better estimates. Dispersants are used more frequently in countries like Great Britain and in many Arabic counties. Again no quantitative results are available to show effectiveness nor lack of such.

TABLE 2 HISTORICAL USE OF DISPERSANTS

SPILL EVENT	YEAR	COUNTRY	AMOUNT SPILLED (t)	DISPERSANT AMOUNT (t)	RESULTS
TORREY CANYON	1967	ENGLAND	119000	10000	LITTLE EFFECTIVENESS, ADVERSE ECOLOGICAL
OCEAN EAGLE	1968	PUERTO R.	12000	60	NO EFFECT
SANTA BARBARA	1969	USA	1000	32	NO EFFECT
ARROW	1970	CANADA	5000	12	NO EFFECT
PACIFIC GLORY	1970	ENGLAND	6300	?	LITTLE EFFECT
SHOWA MARU	1975	SINGAPOR	15000	500	LITTLE EFFECT
JAKOB MAERSK	1975	PORTUGAL	88000	110	LITTLE EFFECT
OLYMPIC ALLIANCE	1975	ENGLAND	2000	220	LITTLE EFFECT
URQUIOLA	1976	SPAIN	100000	2400	LITTLE TO NO EFFECT
AMOCO CADIZ	1978	FRANCE	220000	2500	LITTLE EFFECT
ELENI V	1978	ENGLAND	7500	900	NO EFFECT
CHRISTOS BITAS	1978	ENGLAND	3000	280	LITTLE EFFECT
BETELGEUSE	1979	IRELAND	1000	35	NO EFFECT
IXTOC I	1979	MEXICO	500000	5000	LITTLE EFFECT
SIVAND	1983	ENGLAND	6000	113	LITTLE EFFECT

## DISPERSANTS - LABORATORY STUDIES

A number of laboratory studies have been performed to compare the test results from different apparatus and procedures. A review of these results show that there is poor correlation in effectiveness results between the various test methods.<sup>7</sup> A recent study by the present author has shown that lack of correlation is primarily a function of settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus.<sup>8</sup> Another important factor is that of the oil-to-water ratio in the apparatus. When these two parameters are adjusted to be the same and to larger values, test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests, such as the Mackay test and the Labofina or Warren Springs test, are somewhat higher, but when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Results from a series of tests and after having performed these corrections are shown in Table 3. The effectiveness results from all tests are nearly identical, even though the errors for measurement in the Mackay and Labofina tests are 10 percent or more. The fact that these values are nearly identical may imply that they have some meaning. Just the fact that this phenomena occurs also indicates that energy plays a lesser role than was previously thought. The high energy in the Mackay and Labofina tests only increases the dispersant effectiveness for those oils that disperse naturally.

Early studies were intended to come to an understanding of laboratory effectiveness tests. It had been found that the extant tests yield different results for different dispersant-oil combinations. This was especially true when the oil type was varied, rather than the dispersant type. Dispersants which appeared to be effective on one oil were often quite ineffective on that same oil in another apparatus or test protocol. Additionally, the main test then in the literature, the Labofina (or Warren Springs or Rolling Flask) test and the Mackay (or MNS or Mackay-Nadeau-Steelman) test. The former test uses a separatory funnel with 250 mL of water and 5 mL of oil to test the dispersant. The resulting oil-water ratio is 1:50, a factor that shall later be shown to be of significance. The separatory funnel is rotated at 33 rpm for 10 minutes and then a sample taken after a settling time of 2 minutes and analyzed colorimetrically. The Mackay apparatus, on the other hand, employs 10 mL of oil and 6 L of water to yield an oil-to-water ratio of 1:600. Energy is supplied by a high velocity stream of air. Sampling is done dynamically - no settling time is allowed. The results of the two tests differ with oils - the Mackay test consistently gave higher numbers for heavier oils and especially for very viscous oils. The Mackay effectiveness numbers were also very noisy and had a tendency to be very high or very low. The Labofina effectiveness values, on the other hand, tended to only appear in the mid-range of values - that is around 50%. Attempts to correlate both results with field values were futile. The first effort of EETD was to generate a good data set with both devices to determine what the variances indeed were. The second effort was to test other concepts to see if every device or test yields unique effectiveness values. An oscillating hoop test which employs an oil-to-water ratio of 1:200 using the given protocol was tried. The values produced using this apparatus and test protocol showed values more similar to the Mackay test than to the Labofina, however the data was also noisy like that from the Mackay test. Early conclusions from these study were that lab tests produced unique results based on their protocols and test features. This offered no hope for further understanding of how dispersants did or did not work.

**TABLE 3 EFFECTIVENESS IN DIFFERENT APPARATUS**

OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA	MNS
ADGO	9527	61	52	78	64
	CRX-8	42	40	77	87
	EN 700	67	59	76	93
AMAILIGAK	9527	48	38	86	44
	CRX-8	56	46	73	85
	EN 700	54	39	59	73
ASMB	9527	22	21	31	39
	CRX-8	28	31	34	61
	EN 700	43	43	62	76
ATKINSON	9527	7	18	57	17
	CRX-8	9	10	47	19
	EN 700	8	18	55	22
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	51	35
	CRX-8	23	31	35	76
	EN 700	38	42	70	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	23	6
	CRX-8	9	10	19	9
	EN 700	7	8	23	14
ISSUNGNAC	9527	24	22	61	41
	CRX-8	42	76	35	100
	EN 700	42	60	75	100
LAGO MEDIO	9527	7	8	29	16
	CRX-8	11	15	19	19
	EN 700	10	23	24	27
LUBE OIL	9527	13	19	40	44
	CRX-8	14	24	40	53
	EN 700	13	23	40	80
MOUSSE MIX	9527	9	15	27	30
	CRX-8	11	25	18	26
	EN 700	24	32	23	43
NORMAN WELLS	9527	41	55	65	47
	CRX-8	60	47	70	65
	EN 700	63	53	74	89
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	47	27
	CRX-8	5	16	38	23
	EN 700	17	14	48	37
SYNTHETIC CRUDE	9527	57	50	78	83
	CRX-8	69	55	40	91
	EN 700	61	39	76	88

LEGEND 9527 = COREXIT 9527, CRX-8 = COREXIT CRX-8, EN 700 = ENERSPERSE 700

EETD continued research despite the grim preliminary conclusions noted above. The first effort was the development of a rapid and simple test. The purpose of this was to speed research. About 10 tests per day could be done with the Labofina apparatus then in use and about 6 for the Mackay apparatus. It was obvious that to perform tests for many oils, many dispersants and many different conditions, that a faster test was needed. The development resulted in the Swirling Flask test which employs a standard 125 mL flask with a bottom spout for decanting the sample. Depending on the elaborateness of the test, 30 to 100 runs could be conducted in one day. The protocol chosen for the test was an oil to water ratio of 1:1200 and a settling time of ten minutes. The first results achieved with this new test did not correlate well with either the Mackay or Labofina tests and almost not at all with the oscillating hoop tests. What was dramatically different from all three tests was that results were repeatable within 5%. Results from other tests were as bad as ten times this value.

Testing continued using the new apparatus. The effectiveness of many oils and several dispersants were measured. Values appeared to be correct but low compared to those for other tests. Tests done with the apparatus also showed that there was significant variation in effectiveness with salinity, but over the normal range of 22 to 33 degrees salinity effectiveness variation of only 5 % could be expected. For freshwater effectiveness fell to nearly 0 in all cases. Fluctuation with temperature was not as great as expected or measured with other apparatus. Variation of effectiveness with settling time was measured extensively and it was found that the effectiveness is exponential with time of settling from 0 to 10 minutes and then only changes a small amount after that. This settling time was also measured in the Labofina and Mackay tests and found to be the same. Some of the "noise" in both the latter tests can then be explained by the settling time. In the case of the Labofina, sampling is done at the 2-minute mark a time at which particles are rapidly rising to the surface. Any small error in timing can result in significant variation in amount of oil sampled and subsequently effectiveness. Test results using the swirling flask apparatus are presented in the appendix.

## MECHANISM STUDIES

The first rounds of mechanism studies focused on changed variables in the laboratory tests and observing the effect on dispersant effectiveness. Long-term settling (or rising, depending on the point of view) experiments using the swirling flask apparatus were the first round of experiments to be conducted. It was found that there were about 3 classes of dispersants, those that showed good stability over 48 hours (effectiveness only went down about 20%), those that showed medium stability over the same time period (effectiveness went down about 50%) and those that had poor stability (effectiveness went down about 75%). Most commercial products showed good stability characteristics. This test established three facts about the behaviour of dispersed oil -namely that long term stability is a subject of concern, that different products could have similar stability curves over longer term, and that poor stability also showed up at the 10-minute mark as poor effectiveness. On the positive side, the tests showed that dispersed oil could be somewhat stable in water over a 48-hour period.

Tests conducted on the oscillating hoop, Labofina, Mackay and Swirling Flask test showed one very disturbing finding. All of the first three tests were insensitive to whether the oil was placed in the water or on the oil. Only the swirling flask tested showed no trace of this tendency. In fact, in the case of the three offending apparatus,



it only made a small difference in effectiveness on where the dispersant was placed, with the Labofina showing the least difference, and the Mackay the most. This finding would imply on first glance that in the case of the first 3 apparatus the dispersant can work from the water to the oil rather than vice versa which is the way it would be in nature or in the swirling flask apparatus. This was the first strong indication that the protocols or apparatus were deficient in measuring dispersant effectiveness.

Because the effect that dispersant worked almost as well from the water to the oil as opposed to vice versa in these apparatus, experiments were conducted to see the effect of two main differences between the four apparatus mentioned above, oil-to-water ratio and settling time. As the oil-to-water ratio was increased, the effectiveness went down in all the tests, however became more similar to that of the swirling flask. Similarly for the settling time. In fact, when the four apparatus were run using an oil-to-water ratio of about 1:1000 and a settling time of ten minutes - nearly identical results were produced for many oils - but not for some. Examination of the properties of these oils revealed that all were naturally dispersable. Blanks (samples without dispersants) were run in the respective apparatus and blank values subtracted from the value run with dispersant. In other words, dispersant effectiveness values were corrected for natural dispersion. This finding is very significant in that first all tests can be related and furthermore, the constant result produced by these tests would appear to be a universal effectiveness value. Perhaps this value is the maximum effectiveness which could be expected with the oil-dispersant combination.

At the same time as the above tests were under way, a new test was developed to confirm the effect of oil-to-water ratio. This test was different in concept than any of the other tests and in fact is unique to tests around the world. The test known in EETD labs as the flowing-cylinder test, employs a measuring cylinder with a top and bottom side-spout. Water is circulated from the bottom side-spout through a filter to catch dispersed oil and returned to the cylinder via the top spout. The only dispersing energy supplied to the system is the small amount of energy resulting from the fall of the chemical from the top spout to the oil layer (a distance of about 3 cm). Dispersed oil is continuously removed from the system so that there is no interference of dispersed oil with any processes that may be on-going. The height between the surface of the oil and the withdrawal spout is about 30 cm., this implies that only more stable droplets which do not resurface, are withdrawn from the system. Other droplets will rise to reform a slick. The test was developed for two reasons, one to have a system which could measure oil-to-water ratios to very high values (as large as 1:1,000,000) and to have a system which was not analogous to those others tested so that variables did not include modes of adding energy or operation. The flowing cylinder apparatus yield the same results as the other four devices or tests when they are operated at high oil-to-water ratios and 10 minute settling times. This showed that the previous finding was independent of apparatus mode of operation and that an additional device could produce the same results. The device was used to measure the effect of oil-to-water ratio on dispersant effectiveness. It was found that effectiveness was constant with oil-to-water ratio about 1:800 up to 1:1,000,000 and that effectiveness peaked at 1:600 then slowly fell to a ratio of 1:100. This was confirmed by performing the same experiment in the other three apparatus. It was concluded that this effectiveness was due to a change in mechanism of dispersant action between high oil-to-water ratios and low. In the case of low ratios, the surfactant may interact to form agglomerates and

micelles, thus interfering with the main process by removing surfactant. This would account for the lower effectiveness at the lower ratios. Because dispersion at sea would involve high ratios, laboratory equipment should strive to do the same.

The next round of experiments were the measurement of dispersed oil droplet sizes resulting in the different apparatus. After several hundred measurements, it was found that all apparatus, all oils with all dispersants resulted in the same droplet size of 30 microns VMD. This occurs when apparatus are operated at the optimal settling time and with the optimal oil-to-water ratio as noted above. The meaning of VMD should be explained at this point. In performing particle analysis, two measurements are obtained, particle number and size. The distribution may change from one sample to another. A distribution is a very difficult way to understand test results. For this reason scientist developed the concept of VMD or volume mean diameter which is a single number and is the only way to simplify the interpretation of a complex distribution. It is calculated by summing the volume of particles until the mid-point of the total volume is reached. It is the size at which half the volume of the particles are represented. Because the volume of particles goes up as the cube of particle diameter, average or numbers of particles are meaningless. One 50 micron diameter oil particle contains more oil than 1,000,000 - 1 micron droplets.

The significance of the droplet-size finding is that there exists a distribution size of oil droplet sizes, 30 microns VMD as found in the experiments, which are stable and to which all oil spill dispersions will tend. The significance of this finding is two-fold, first further measurement of sizes is meaningless since the same number is the result and secondly that dispersions of any oil are as stable as the next. The only variance noted in stability is caused by the dispersant.

In tandem with the laboratory studies, analysis of historical field trials was performed. In 16 series of field trials in which 106 slicks had been laid, effectiveness averaged only 30%. Significantly, the variation in values was very high. Many trials reported percentages around 20%, however some trials reported very high values and many very low values. The range of values alone indicated problems. Experimenters in the past 7 years generally did not try to estimate effectiveness, noting the difficulties in doing so. Effectiveness in these cases was said to be high, low or medium, depending on visual observations and the peak concentrations observed at the spill test. Reexamination of the data from earlier trials showed several problems; data did not correlate well between experiments generally in terms of peak, average or location of concentrations, distribution of the oil over the slicks showed no pattern and effectiveness claimed did not correlate well with the concentrations of oil found.

Observations and re-analysis of remote sensing data showed that additional problems with dispersants were operative including, herding of the oil and direct passage of dispersant into the water column. Initial thinking was that rendering dispersants more oleophilic would cure both of these problems. Studies also began in EETD labs to examine possible formulation changes for dispersants. Early work focused on "doping" existing dispersant formulations with surfactants that would render the mixture more oleophilic. This did not result in success because as can be seen later, dispersant technology is very critical in terms of oil/water solubility.

Investigations into the basics of surfactant technology has brought some revelations into the whole issue of dispersants and their effectiveness. Surfactants can be rated on the basis of the balance between their water soluble (hydrophilic) portion

and their oil soluble (lipophilic) parts. A scale was developed to express this for non-ionic surfactants and these were rated on a scale of 0 to 20 where everything below 10 is oil soluble and everything above 10 is water soluble but also surfactants with HLB's less than 10 stabilize water-in-oil emulsions and those above oil-in-water emulsions. Those with HLB of near 10 are dispersants, and this in fact by a series of tests is found to be very critical for some classes of surfactants.

Existing dispersants were found to consist of three active ingredients or surfactants - a high HLB one typically around 15 and a low HLB one, typically around 5 HLB, and an ionic surfactant whose HLB would be about 40. All of the commercial dispersants since 1968 have had a very similar formulation, only the solvents and specific choices of these surfactants vary. The formulation is in fact, provided in general terms by surfactant suppliers. The formulation was first developed as a low-toxicity domestic degreasing or oil-removing formula. The logic behind choosing the two surfactants with HLB of 5 and 15 was that the different geometric configurations would cause tighter packing than by the use of one surfactant alone. The second presumption is that mixing surfactants of high and low HLB can be done to produce a stable product with an average HLB of around 10. The ionic surfactant is present to give even tighter packing and its HLB is generally not counted in designing a formulation. As later studies show, each of these assumptions is incorrect in open systems such as in the use of dispersants at sea.

One of the problems examined by a number of researchers was that of herding or pushing aside of the oil by the dispersant. This was observed at a number of field trials and actual applications. Before 1980 or so most people believed that this phenomena was actually dispersants working very rapidly. Unfortunately some people still cling to the belief. The only actual research on herding on open systems was done by Brown of Esso Resources who was able to quantify herding rates and velocities. Tests in the EETD laboratory showed that herding occurred at all times on thin slicks with most dispersants. Once waves were increased from 2 to 3 cm. herding ceased. Literature on the phenomenon is scarce, however early work by E. Nagy has also shown that tests of a herding agents showed similar limitations. The finding is logical in that the spreading energy of a chemical is weak compared to gravity and that the two would be equal at a gravitational difference of 2 to 5 cm. This also explains why herding was not universally observed at spill scenes. Work done by Betcher on herding has shown that surfactants with HLB's greater than 10 do herd and that this effect increases with increasing HLB. This indicates that either the dispersant has high HLB's or that the surfactants are separating to cause herding. The latter is largely confirmed by analysis of remote sensing data at the Beaufort Sea trials which shows surfactant on the sea surface slowly separating from the slick. Secondly, and more importantly, the formulator of a major dispersant revealed that their herding agent has an identical surfactant as the high HLB one in the dispersant!

Thus evidence is mounting that traditional surfactant mixtures are not stable. Some additional information was found in the lab by performing simple analysis on water in dispersant experiments, it was found that this contained significant amounts of surfactant whether or not dispersion occurred.

The solvents in the old dispersant mixtures were aromatic petroleum solvents and were thus quite toxic to aquatic life. After the TORREY CANYON incident, this was changed to less toxic petroleum solvents. The generation of "no mix" dispersants saw

this change to butyl cellosolve and polyols. Butyl cellosolve is now regarded as a chemical with potential health problems. Potential for improvement could also include solvent change because the current solvents have a tendency to move the surfactants into the water rather than accommodate them to the oil.

Investigation into dispersant formulation again continued with simple mixtures showing improved performance. Rendering the existing mixtures more oleophilic resulted in improved performance for lighter oils. Significant lessons were learned about dispersant action mechanisms: that surfactant HLB is much more critical than originally thought (one surfactant family showed a high effectiveness with an HLB of 10.2, whereas the member with one more methylene group showed no effectiveness and caused the oil to form emulsion), that only surfactants with HLB of 10 showed promise, that mixtures of surfactants to yield an average HLB of 10 using high and low HLB products were not as effective as single surfactants nor did their group effectiveness indicate as high an effectiveness as would be expected, that ionic surfactants by themselves had no effectiveness and simply went into the water, and that most solid surfactants did not work, largely because they would not mix with the oil.

In 1989, a joint study with the U.S. MMS was begun to examine another phenomenon, that of the accelerated weathering caused by dispersants.<sup>9</sup> it was known that dispersants caused accelerated weather of the oil, but the extent to which this might occur was not. Two series of experiments were run, first using standard dispersant laboratory effectiveness apparatus, the Mackay, the Labofina and the Swirling Flask test. The method of performing the experiment was to measure oil in the water column and left on the surface so that a mass balance could be achieved. In oils not treated with dispersant all mass could be accounted for within the experimental error of about 5%. For dispersant-treated oils the loss of mass was taken as the amount lost due to accelerated weathering. This round of experiments resulted in the findings that the amount of weathering was dependent on the oil type. The amount removed from the oil over above that oil not dispersant treated, was about half of the maximum amount lost through normal weathering on exposure for long periods of time. For a series of common oils this averaged about 10%, but could be as much as 20% for a very light oil. The second phase of the experiment was to analyze both the oil in the water and the oil remaining on top by gas chromatography and compare this to the starting oil. Using chromatographic analysis, it was found that accelerated weathering again occurred to about the same percentage as found before. In addition to this, a very important discovery was made, that the composition of the oil in the water column and on the surface had compositional changes other than those caused by weathering alone. It was found more n-alkanes were taken into the water column for those chain lengths corresponding to the same chain length of the oleophilic portion of the surfactant. Surface oil was deficient in these same compounds, confirming the hypothesis that this was absorption to the oleophilic portion of the surfactant. The oil on the surface contained a higher amount of n-alkanes of longer chain lengths than did the starting oil, showing that separation of the oil does occur to a certain extent and that certain portions, eg. longer molecules, are less dispersable. These findings are significant, showing that longer-chain surfactants may be necessary to achieve greater dispersion, that surface means of measuring dispersant effectiveness means must compensate for the accelerated weathering and that there are lesser dispersable components of the oil.

The findings of the mechanism studies can be summarized as follows:

1. That separation of mixed surfactant systems occurs,
2. That herding is limited to low waves, <2 to 3 cm,
3. Herding in existing dispersants is largely due to high HLB fractions of mixed surfactant systems currently in use,
4. Dispersant use results in accelerated weathering of the oil,
5. Dispersant draw more of the oils compounds that correspond to their oleophilic chain lengths into the water,
6. That long chain lengths and perhaps other components of the oil are dispersed less than shorter chain lengths.
7. That the droplet sizes produced by most dispersants and most oils in most apparatus, may have the same size distribution

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OIL	DISPERSANT	AVERAGE	EFFECTIVENESS PERCENT		
			% PREMIXED	% 1 DROP	% 2 DROPS
ADGO	C 9527	61	61	82	41
ADGO	CRX-8	39	61	31	26
ADGO	ENER 700	59	76	53	47
ADGO	DASIC	8	11	7	5
AMAULIGAK	C 9527	45	50	36	49
AMAULIGAK	CRX-8	50	61	51	37
AMAULIGAK	ENER 700	62	65	62	59
AMAULIGAK	DASIC	28	23	40	22
AMAULIGAK	DREW	0	TL	TL	TL
AMAULIGAK	C 9550	0	TL	TL	TL
AMAULIGAK	BQ	60	72	52	57
AMAULIGAK	II	0	22	TL	TL
ARABIAN LIGHT	C 9527	17	31	16	3.3
ARABIAN LIGHT	CRX-8	9	15	8.6	4.8
ARABIAN LIGHT	ENER 700	22	16	27	23
ARABIAN LIGHT	DASIC	33	24	36	40
ARABIAN LIGHT	BQ	42	28	54	43
ASMB	C 9527	33	42	28	28
ASMB	CRX-8	45	57	43	35
ASMB	ENER 700	51	68	51	35
ASMB	DASIC	24	18	27	28
ASMB	DREW LT	0	TL	TL	TL
ASMB	C 9550	0	TL	TL	TL
ASMB	BQ	79	81	82	73
ASMB	II	18	49	5	0
ASMB	WELLAID 3315	14	8	12	21
ASMB	BP1100WD	12	6	14	17
ASMB	BP1100X	7	1	10	11
ATKINSON	C 9527	39	59	31	27
ATKINSON	CRX-8	31	67	19	7
ATKINSON	ENER 700	73	79	75	66
ATKINSON	DASIC	49	33	61	53
AVALON J-34	C 9527	11	18	7.5	8
AVALON J-34	CRX-8	5	7.6	5.3	3.3
AVALON J-34	ENER 700	11	15	12	7
AVALON J-34	DASIC	16	8	18	21
AVALON J-34	BQ	10	11	11	7.1
AVALON ZONE 4	C 9527	10	14	10	5.7
AVALON ZONE 4	CRX-8	7	14	4.2	3.1
AVALON ZONE 4	ENER 700	26	25	27	27
AVALON ZONE 4	DASIC	30	12	40	38
AVALON ZONE 4	BQ	13	16	14	10
BENT HORN	C 9527	17	12	17	21
BENT HORN	CRX-8	20	15	19	27

OIL	DISPERSANT	AVERAGE	EFFECTIVENESS PERCENT		
			% PREMIXED	% 1 DROP	% 2 DROPS
BENT HORN	ENER 700	23	10	18	42
BENT HORN	DASIC	35	14	43	48
BUNKER C	C 9527	1	2.3	1.1	1
BUNKER C	CRX-8	2	3.8	1.3	0.9
BUNKER C	ENER 700	1	0.9	1.9	0.8
BUNKER C	DASIC	2	2.1	2.9	0.6
BUNKER C	BQ	1	1.4	1.4	0.8
BUNKER C LIGHT	C 9527	1	0.6	1	0.4
BUNKER C LIGHT	CRX-8	1	0.7	0.9	0.7
BUNKER C LIGHT	ENER 700	1	0.7	2	1.5
BUNKER C LIGHT	DASIC	1	0.6	1.7	1.3
BUNKER C LIGHT	BQ	2	1.6	2.6	0.8
CALIFORNIA CRUDE (11.0)	C 9527	1	0.5	1.1	0.9
CALIFORNIA CRUDE (11.0)	CRX-8	1	2.3	1.2	0.8
CALIFORNIA CRUDE (11.0)	ENER 700	1	0.4	2.7	0.8
CALIFORNIA CRUDE (11.0)	DASIC	1	0.2	2.2	0.8
CALIFORNIA CRUDE (11.0)	BQ	1	0.4	2.2	1.7
CALIFORNIA CRUDE (15)	C 9527	1	1.3	0.7	0.3
CALIFORNIA CRUDE (15)	CRX-8	1	0.4	0.8	0.6
CALIFORNIA CRUDE (15)	ENER 700	1	0.9	0.9	1
CALIFORNIA CRUDE (15)	DASIC	2	0.8	3	3.3
CALIFORNIA CRUDE (15)	BQ	1	1.4	1.3	0.8
COHASSET	C 9527	95	88	100	98
COHASSET (11.2% W)	C 9527	96	88	99	100
COHASSET (25.6% W)	C 9527	88	75	92	97
COHASSET (28.1% W)	C 9527	90	74	97	100
COLD LAKE BITUMEN	C 9527	2	1.9	2.3	0.4
COLD LAKE BITUMEN	CRX-8	1	1.1	2.1	0.6
COLD LAKE BITUMEN	ENER 700	1	0.9	1.4	0.4
COLD LAKE BITUMEN	DASIC	1	1	1	0.3
COLD LAKE BITUMEN	BQ	1	1.1	1.5	0.3
ENDICOTT	C 9527	7	17	2.3	2.8
ENDICOTT	CRX-8	8	20	1.3	2.4
ENDICOTT	ENER 700	6	10	2.4	6.4
ENDICOTT	DASIC	14	8.1	15	18
ENDICOTT	BQ	13	18	6.9	13
ENDICOTT (7.5% W.)	C 9527	3	3	3	3
ENDICOTT (7.5% W.)	CRX-8	4	5	3	3
ENDICOTT (7.5% W.)	ENER 700	6	4	6	9
ENDICOTT (7.5% W.)	DASIC	4	1	1	11
ENDICOTT (7.5% W.)	BQ	6	4	6	7
ENDICOTT (11.7%W.)	C 9527	2	2	2	2
ENDICOTT (11.7%W.)	CRX-8	2	2	3	2
ENDICOTT (11.7%W.)	ENER 700	6	2	9	6

OIL	DISPERSANT	EFFECTIVENESS PERCENT			
		AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
ENDICOTT (11.7%W.)	DASIC	3	1	3	4
ENDICOTT (11.7%W.)	BQ	4	1	6	6
FEDERATED	C 9527	25	41	24	11
FEDERATED	CRX-8	31	50	26	16
FEDERATED	ENER 700	40	41	56	22
FEDERATED	DASIC	38	23	55	35
FEDERATED	BQ	64	66	85	42
HIBERNIA	C 9527	6	13	1.9	1.8
HIBERNIA	CRX-8	6	14	2.6	2
HIBERNIA	ENER 700	10	7.3	10	14
HIBERNIA	DASIC	14	8.6	18	16
HIBERNIA	BQ	9	7.8	12	6
HIBERNIA	WELLAID 3315	4	3	4	4
HIBERNIA (15.4% W)	C 9527	4	6.1	2.3	2.5
HIBERNIA (15.4% W)	CRX-8	3	5.8	1	2
HIBERNIA (15.4% W)	ENER 700	8	5	11	7.5
HIBERNIA (15.4% W)	DASIC	7	1	8	11
HIBERNIA (15.4% W)	BQ	5	4	6	4
ISSUNGAK	C 9527	66	70	93	35
ISSUNGAK	CRX-8	60	58	75	47
ISSUNGAK	ENER 700	62	51	79	57
ISSUNGAK	DASIC	51	31	60	61
ISSUNGAK	BQ	77	77	69	84
LAGO MEDIO	C 9527	5	9.5	3.6	1.5
LAGO MEDIO	CRX-8	5	13	1.8	1.4
LAGO MEDIO	ENER 700	13	11	21	5.9
LAGO MEDIO	DASIC	15	4.1	18	24
LAGO MEDIO	BQ	18	22	25	6.3
MOUSSE MIX	C 9527	6	9	5	3
MOUSSE MIX	CRX-8	9	15	8	5
MOUSSE MIX	ENER 700	14	10	19	13
MOUSSE MIX	DASIC	17	9	22	20
MOUSSE MIX	BQ	18	25	17	12
MOUSSE MIX	II	6	15	3	0
NORMAN WELLS	C 9527	36	51	40	17
NORMAN WELLS	CRX-8	43	60	38	30
NORMAN WELLS	ENER 700	51	73	26	53
NORMAN WELLS	DASIC	26	19	33	27
NORMAN WELLS	DREW LT	0	TL	TL	TL
NORMAN WELLS	C 9550	0	TL	TL	TL
NORMAN WELLS	BQ	77	83	80	68
NORMAN WELLS	II	0	33	TL	TL
PANUK	C 9527	96	95	95	97
PANUK	CRX-8	78	100	62	71



OIL	DISPERSANT	AVERAGE	EFFECTIVENESS PERCENT		
			% PREMIXED	% 1 DROP	% 2 DROPS
PANUK	ENER 700	96	93	97	99
PANUK	DASIC	40	44	38	37
PANUK	BQ	100	100	100	99
PANUK (47.4% W)	C 9527	99	96	100	100
PANUK (53.2% W)	C 9527	99	96	100	100
PRUDHOE BAY	C 9527	13	19	13	7
PRUDHOE BAY	CRX-8	13	23	9	6
PRUDHOE BAY	BQ	32	43	29	24
PRUDHOE BAY	ENER 700	35	48	26	31
PRUDHOE BAY	DASIC	11	14		18
PRUDHOE BAY (1989)	C 9527	7	13	5.8	2.5
PRUDHOE BAY (1989)	CRX-8	7	15	3.2	3.9
PRUDHOE BAY (1989)	ENER 700	10	15	3.1	13
PRUDHOE BAY (1989)	DASIC	14	11	18	13
PRUDHOE BAY (1989)	BQ	15	25	4.8	16
PRUDHOE BAY (1989)	WELLAID 3315	4	3	5	3
PRUDHOE BAY (89) (7.6%)	C 9527	6	9	3	5
PRUDHOE BAY (89) (7.6%)	CRX-8	6	13	3	3
PRUDHOE BAY (89) (7.6%)	ENER 700	16	8	25	16
PRUDHOE BAY (89) (7.6%)	DASIC	16	12	19	18
PRUDHOE BAY (89) (7.6%)	BQ	19	29	18	10
PRUDHOE BAY (89) (14.5%)	C 9527	4	5	4	3
PRUDHOE BAY (89) (14.5%)	CRX-8	4	8	2	3
PRUDHOE BAY (89) (14.5%)	ENER 700	8	4	6	14
PRUDHOE BAY (89) (14.5%)	DASIC	10	2	14	13
PRUDHOE BAY (89) (14.5%)	BQ	9	7	15	5
SOUTH LOUISIANA CRUDE	C 9527	31	53	19	21
SOUTH LOUISIANA CRUDE	CRX-8	36	55	33	19
SOUTH LOUISIANA CRUDE	ENER 700	48	31	75	37
SOUTH LOUISIANA CRUDE	DASIC	42	27	50	50
SOUTH LOUISIANA CRUDE	BQ	62	71	80	35
SYNTHETIC CRUDE	C 9527	63	77	88	25
SYNTHETIC CRUDE	CRX-8	41	49	41	34
SYNTHETIC CRUDE	ENER 700	61	69	69	45
SYNTHETIC CRUDE	DASIC	25	23	30	21
SYNTHETIC CRUDE	BQ	55	89	42	34
TERRA NOVA CRUDE	C 9527	16	29	13	6.5
TERRA NOVA CRUDE	CRX-8	11	22	5.2	6.5
TERRA NOVA CRUDE	ENER 700	28	21	38	24
TERRA NOVA CRUDE	DASIC	40	19	58	44
TERRA NOVA CRUDE	BQ	40	40	53	27
TRANSMOUNTAIN BLEND	C 9527	8	14	6	3.1
TRANSMOUNTAIN BLEND	CRX-8	8	13	5.3	6.6
TRANSMOUNTAIN BLEND	ENER 700	28	17	43	25

OIL	DISPERSANT	AVERAGE	EFFECTIVENESS PERCENT		
			% PREMIXED	% 1 DROP	% 2 DROPS
TRANSMOUNTAIN BLEND	DASIC	27	11	40	31
TRANSMOUNTAIN BLEND	BQ	19	25	18	15
USED MOTOR OIL	C 9527	33	42	31	27
USED MOTOR OIL	CRX-8	31	39	31	23
USED MOTOR OIL	ENER 700	36	47	32	30
USED MOTOR OIL	DASIC	29	29	27	31
USED MOTOR OIL	BQ	36	42	41	24

**EXPLANATION OF TESTS**

**PREMIXED - REFLECTS THE LARGEST AMOUNT DISPERSED  
WHEN DISPERSANT MIXED INTO OIL AT RATIO 1:25**

**1-DROP - REFLECTS LARGEST AMOUNT DISPERSED AT  
A DISPERSANT TO OIL RATIO OF 1:10**

**- TEST MEASURES HOW OIL/DISPERSANT COMBINATION  
FUNCTIONS WITH REAL APPLICATION**

**2-DROP - REFLECTS LARGEST AMOUNT DISPERSED AT  
A DISPERSANT TO OIL RATIO OF 1:10 BUT DELIVERED IN  
TWO DROPS**

**- TEST MEASURES THE HERDING EFFECT OF THE  
OIL/DISPERSANT COMBINATION WHEN COMPARED  
TO THE ONE DROP TEST**

**BQ AND II ARE EXPERIMENTAL DISPERSANTS MADE BY EETD**

**TL = TOO LOW TO MEASURE**